



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C09K 5/04</b>	<b>A1</b>	(11) International Publication Number: <b>WO 97/34961</b> (43) International Publication Date: 25 September 1997 (25.09.97)
<p>(21) International Application Number: PCT/US97/04592</p> <p>(22) International Filing Date: 21 March 1997 (21.03.97)</p> <p>(30) Priority Data: 60/013,946 22 March 1996 (22.03.96) US</p> <p>(71)(72) Applicant and Inventor: GOBLE, George, H. [US/US]; 286 West Navajo, West Lafayette, IN 47906 (US).</p> <p>(74) Agents: BROWNING, Clifford, W. et al.; Woodard, Emhardt, Naughton, Moriarty &amp; McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).</p>		<p>(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>

(54) Title: DROP-IN SUBSTITUTES FOR 1,1,1,2-TETRAFLUOROETHANE (R-134a) REFRIGERANT

(57) Abstract

A group of refrigerant fluids that may be combined in novel ways to produce several excellent "drop-in" substitutes for R-134a refrigerant. Performance is increased by constructing a zeotropic mixture of refrigerants, such that a single boiling point (of R-134a) is replaced by a "temperature glide" between the mixture's "bubble point" and "dew point". The temperature glide causes the phase change area in the condenser to be larger than with a single component refrigerant such as R-134a, thereby increasing heat rejection of the condenser, which lowers head pressures, and increases capacities and efficiencies compared to R-134a. Components are also selected to attempt to reduce the overall critical temperature of the mixture of refrigerants, also increasing performance and lowering head pressures under hot conditions with undersized condensers. Finally, a small amount of a mineral oil miscibility improver may be added, not to return mineral oil from the evaporator as in R-12 systems, but to keep waxes, tars, and other contaminants in the system that may have arisen from the manufacturing process (such as wax coatings on the motor windings in a hermetic compressor, or "tar" from valve packing) soluble.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DROP-IN SUBSTITUTES FOR  
1,1,1,2-TETRAFLUOROETHANE (R-134a)  
REFRIGERANT

The present invention relates to refrigerants generally, and more  
5 specifically to a mixture of refrigerants that may be substituted for 1,1,1,2-  
tetrafluoroethane (R-134a) refrigerant.

BACKGROUND OF THE INVENTION

In order to provide a more compact format for identifying mixtures of  
refrigerants in the following discussions, mixtures of refrigerants will be  
10 listed in the form of:

R-ABC/DEF/GHI N0/N1/N2

which represents a mixture of refrigerants (fluids) R-ABC, R-DEF, and R-  
GHI where N0, N1, and N2 are the weight percentages of each component  
refrigerant fluid, and  $N0+N1+N2 = 100$  percent; or in the form of:

15 R-ABC/DEF/GHI N0-N0'/N1-N1'/N2-N2'

which is similar, but specifies ranges of the weight percentages each of the  
component refrigerant fluids, with the total of the weight percentages being  
100 percent.

20 Zeotropic (nonazeotropic) mixtures of refrigerants will change  
composition if they are allowed to leak as vapor phase from a container  
containing all components of the refrigerant mixture in both vapor and  
liquid phases. Single component and azeotropic mixtures of refrigerants  
do not change composition appreciably from vapor leakage. Single  
component and azeotropic mixtures of refrigerants have only one boiling  
25 point temperature for a given pressure, provided the refrigerant exists as  
both liquid and vapor states in the container. Zeotropic mixtures of

refrigerants will boil over a range of temperatures at a given pressure. As the temperature is raised, the point at which the first bubbles appear (constant pressure) in the liquid is known as the "bubble point," which is roughly analogous to the boiling point of a single component or an  
5 azeotropic mixture. Starting in a vapor phase and lowering the temperature (at a constant pressure) to the point where the first droplet of liquid forms defines what is known as the "dew point" of the mixture of refrigerants. The difference between the bubble point temperature and the dew point temperature is known as the temperature "glide". A pressure  
10 gauge connected to a cylinder containing a zeotropic mixture of refrigerants will read the bubble point pressure for the corresponding temperature of the refrigerant mixture.

Under the Montreal Protocol, as amended, United States laws (1990 Clean Air Act), and U.S. Environmental Protection Agency rules, the  
15 production and importing of dichlorodifluoromethane (CFC-12 or R-12) refrigerant ended on December 31, 1995. Additionally, only 15% of the 1989 baseline amounts of chlorinated fluorocarbons (CFCs) was allowed to be produced or imported into the U.S. during the year 1995, adjusted on an ozone depletion factor basis. R-12 was the major share of that production.

20 With the effective date of the ban on U.S. R-12 production and importing having passed (December 31, 1995), one industry option has been to retrofit R-12 refrigeration or air conditioning systems, both stationary and automotive, to R-134a (tetrafluoroethane). The mineral oils used in R-12 systems are completely immiscible in R-134a. The industry  
25 has therefore developed new oils, which are either polyalkylene glycol (PAG) based (for automotive) or polyol ester (POE) based (stationary refrigeration and some automotive retrofit).

While PAG oils are good lubricants, and are miscible in R-134a at typical evaporator temperatures, they have two main problems. First, most PAG oils cannot tolerate even minute traces of residual chlorides that remain in the R-12 refrigeration or air conditioning systems that have been  
5 purged of R-12. These chlorides are dissolved in the small amount of mineral oils which cannot be flushed out or are in coatings on the inside of aluminum piping (aluminum chloride from previous R-12) or are dissolved in rubber hoses. The presence of chlorides greatly accelerates the breakdown of most PAG oils.

10 It has been reported in the literature that test systems that were flushed with R-11 (trichlorofluoromethane) and then retrofitted to PAG oil and R-134a, sustained catastrophic compressor failures within one week due to oil breakdown. R-11 has a greater affect on PAG oil breakdown than does R-12. It was common practice in the automotive air conditioning  
15 service industry, into the early 1990s, to flush R-12 systems with R-11 to remove contaminants. The traces of R-11 remaining do not interfere with R-12 operation, but could cause premature failures if R-12 systems are ever retrofitted to R-134a and PAG oils.

20 Compressors manufactured for R-12 and mineral oil use were often constructed with a paraffin based wax coating on the motor windings as an aid to building the motor without breaking the wire during the motor winding phase of the construction. When retrofitted to R-134a and POE oils, the paraffin would sometimes come off the windings, and not dissolve in the R-134a refrigerant and POE oils, and circulate through the system as  
25 solids and plug up the refrigerant metering device, usually a capillary tube, causing the system to fail. R-12 (or a substitute with adequate mineral oil miscibility) and mineral oil just dissolve the pieces of paraffin wax that

-4-

come off the motor windings and therefore do not clog the refrigerant metering device.

Finally, the low critical temperature of R-134a (214.07 degrees Fahrenheit) verses the critical temperature of R-12 (233.26 degrees Fahrenheit) can cause abnormally high head pressures in hot ambient conditions in systems designed for R-12. For automotive applications, stopped traffic or hot climates can cause a reduction in R-134a performance. Systems designed for R-134a often increase the size of the condenser about 50 percent over the size similarly designed R-12 system condenser. Stationary systems, such as vending machines, now retrofitted to R-134a, may see high head pressure and low performance problems when the condenser becomes slightly fouled by dirt and dust. R-12 systems can run much longer between cleanings to remove dust and dirt from the condenser than similar systems converted to R-134a.

R-406A is a known ternary mixture of refrigerants, consisting of isobutane (R-600a), chlorodifluoroethane (R-142b), and chlorodifluoromethane (R-22), that provides a "drop-in" substitute for dichlorodifluoromethane (R-12) refrigerant. R-406A is described in U.S. Patent Nos. 5,151,207 and 5,214,929, the disclosures of which are incorporated herein by reference.

If one must convert an existing R-12 refrigeration or air conditioning system to another refrigerant due to the Montreal Protocol mandated phaseout of R-12 refrigerant, it is usually far preferable to use a refrigerant mixture with adequate miscibility with mineral oils used by R-12 systems, such as R-406A (R-600a/142b/22 4/41/55) or GHG-X4 (R-600a/124/142b/22 4/28.5/16.5/51) than to attempt to retrofit to R-134a. However, one may have followed the industry recommended choice and already retrofitted said systems to R-134a or purchased a new system that

was manufactured for R-134a refrigerant, using lubricants that are miscible with R-134a such as POE or PAG oils.

To date, the oils used in new or retrofitted R-134a refrigeration and air conditioning systems (PAG and some POE) are adversely affected by chlorinated refrigerants (HCFCs), with the PAG oils being affected more than the POE oils. Once installed in a refrigeration or air conditioning system, PAG or POE oils are virtually impossible to completely remove from a system, especially from the compressor. If said systems were then recharged with chlorine containing refrigerants, such as R-406A or GHG-X4 and R-12 compatible mineral oils, some amount of the PAG or POE oils would remain and would be destroyed, creating contamination and system failures. A better performing refrigerant is needed that can be "drop-in" substituted for R-134a in R-134a refrigeration and air conditioning systems, and that is also compatible with oils used by R-134a refrigeration and air conditioning systems.

There are a few existing refrigerants that can be "drop-in" substituted for R-134a in R-134a refrigeration and air conditioning systems, such as OZ-12, HC-12a, and ES-12r. However, these mixtures are composed entirely of hydrocarbons (typically R-600a/290 40/60) and are extremely flammable. Hydrocarbon mixtures are outlawed in many states and by US EPA as "unacceptable" for use as a replacement for R-12 in all but a few specialized uses. These hydrocarbon refrigerants contain no chlorinated compounds, so they do not destroy oils used in R-134a systems.

## SUMMARY OF THE INVENTION

In summary, I have discovered a group of refrigerant fluids, which are listed in Table 1, that may be combined in novel ways to produce

several excellent "drop-in" substitutes for R-134a refrigerant. Performance is increased by constructing a zeotropic mixture of refrigerants, such that a single boiling point (of R-134a) is replaced by a "temperature glide" between the mixture's "bubble point" and "dew point". The temperature glide causes the phase change area in the condenser to be larger than with a single component refrigerant such as R-134a, thereby increasing heat rejection of the condenser, which lowers head pressures, and increases capacities and efficiencies compared to R-134a. Components are also selected to attempt to reduce the overall critical temperature of the mixture of refrigerants, also increasing performance and lowering head pressures under hot conditions with undersized condensers. Finally, a small amount of a mineral oil miscibility improver may be added, not to return mineral oil from the evaporator as in R-12 systems, but to keep waxes, tars, and other contaminants in the system that may have arisen from the manufacturing process (such as wax coatings on the motor windings in a hermetic compressor, or "tar" from valve packing) soluble. In R-12 mineral oil systems, these contaminants readily dissolve in mineral oils, causing no problems. In R-134a systems, the waxes and tars may not be soluble in POE or PAG oils and may turn into solids, and plug up the refrigerant metering device. The addition of a very small amount of a mineral oil miscibility improver prevents these contaminants from becoming solid and plugging the system.

One embodiment of the present invention is the creation of "drop-in" substitutes for R-134a from novel mixtures of components from Table 1.

It is also an object of the present invention to provide a "drop-in" refrigerant substitute for R-134a that provides an acceptable level of cooling in low, medium, and high temperature applications where R-134a is now in use.



It is also an object of the present invention to provide a "drop-in" refrigerant substitute for R-134a that keeps a small amount of system contaminants, such as tars and waxes, soluble in the refrigerant/lubricant mixture, so said contaminants do not plug small openings, such as refrigerant metering devices

It is also an object of the present invention to provide a "drop-in" substitute refrigerant for R-134a that causes very little global warming damage.

It is also an object of the present invention to provide a "drop-in" substitute refrigerant for R-134a that causes zero stratospheric ozone damage.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments described below and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the described embodiments, and such further applications of the principles of the invention as described therein being contemplated as would normally occur to one skilled in the art to which this invention relates.

Boiling points (BP), and critical temperatures (Crit) in Table 1 are in degrees Fahrenheit and are taken from the November 1993 "NIST Database 23: NIST REFPROP v4.0", available from U.S. Department of Commerce, Technology Administration, National Institute of Standards and Technology (NIST), Standard Reference Data Program, Gaithersburg MD 20899, and the "January 1996 ARTI Refrigerant Database", available from

Engineering Consultant, 10887 Woodleaf Lane, Great Falls VA 22066-3003. Molecular weights (MW) are taken from the same sources.

Table 1

	R-num	Formula	Name	BP	Crit	MW
	R-227ea	CF <sub>3</sub> CHFCF <sub>3</sub>	1,1,1,2,3,3,3-heptafluoropropane*	2.5	215.37	170.0
5	R-134a	CF <sub>3</sub> -CH <sub>2</sub> F	1,1,1,2-tetrafluoroethane	-15.07	214.07	102.0
	R-143a	CF <sub>3</sub> -CH <sub>3</sub>	1,1,1-trifluoroethane	-53.23	163.58	84.04
	R-125	C <sub>2</sub> HF <sub>5</sub>	pentafluoroethane	-55.43	151.12	120.0
	R-E125	CFH <sub>2</sub> -O-CF <sub>3</sub>	difluoromethyltrifluoromethyl ether	-41.9	176.7	136.0
10	R-E143a	CH <sub>3</sub> -O-CF <sub>3</sub>	methyl trifluoromethyl ether	-10.8	220.8	100.04
	R-E227ca2	CHF <sub>2</sub> -CF <sub>2</sub> -O-CF <sub>3</sub>	1-(trifluoromethoxy)-1,1,2,2-tetrafluoroethane	26.3	186.0	238.3
15	R-245cb	CH <sub>3</sub> -CF <sub>2</sub> -CF <sub>3</sub>	1,1,1,2,2-pentafluoropropane	0.3	224.5	134.0
	R-600a	C(CH <sub>3</sub> ) <sub>3</sub>	isobutane	10.83	274.46	58.12
	R-290	C <sub>3</sub> H <sub>8</sub>	propane	-43.75	206.06	44.10
	R-E170	CH <sub>3</sub> -O-CH <sub>3</sub>	dimethyl ether (DME)	-12.7	263.8	46.07
20	R-1270	CH <sub>3</sub> CH=CH <sub>2</sub>	propylene	-53.8	198.4	42.07
	R-1216	CF <sub>2</sub> =CFCF <sub>3</sub>	hexafluoropropene	-20.2	unknown	150.0
	R-218	C <sub>3</sub> F <sub>8</sub>	perfluoropropane	-34.15	161.4	188.0
	R-C318	C <sub>4</sub> F <sub>8</sub>	octafluorocyclobutane	19.42	239.6	200.4
	R-C270	C <sub>3</sub> H <sub>6</sub>	cyclopropane	-27.2	256.3	42.1
25	R-152a	CH <sub>3</sub> CHF <sub>2</sub>	1,1-difluoroethane	-12.37	236.39	66.05
	R-600	C <sub>4</sub> H <sub>10</sub>	n-butane	31.03	305.62	58.12
	R-32	CH <sub>2</sub> F <sub>2</sub>	difluoromethane	-61.15	172.78	52.02
	R-134	CHF <sub>2</sub> CHF <sub>2</sub>	1,1,2,2-tetrafluoroethane	-3.66	246.11	102.03
	R-116	CF <sub>3</sub> CF <sub>3</sub>	hexafluoroethane	-108.7	67.8	138.0124
	R-23	HCF <sub>3</sub>	trifluoromethane	-115.65	78.71	70.01
30	R-7146	SF <sub>6</sub>	sulfur hexafluoride	-82.8	114.0	146.054
	R-CE216	-CF <sub>2</sub> -CF <sub>2</sub> -O-CF <sub>2</sub> -	hexafluoro-oxetane	-20.4	191.1	166.0228
	R-C216	-CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -	hexafluorocyclopropane	-24.7	unknown	150.0234
35	R-CE216ca1	-CF <sub>2</sub> -O-CF <sub>2</sub> -O-CF <sub>2</sub> -	hexafluorodioxetane	-7.8	194.0	182.0222
	R-E218	CF <sub>3</sub> -CF <sub>2</sub> -O-CF <sub>3</sub>	1-(trifluoromethoxy)-1,1,2,2,2-pentafluoroethane	unknown	unknown	204.02
40	R-E218ca12	CF <sub>3</sub> -O-CF <sub>2</sub> -O-CF <sub>3</sub>	bis(trifluoromethoxy)-difluoromethane	unknown	unknown	220.0191

\*At the present time, only the 1,1,1,2,3,3,3-heptafluoropropane isomer is available in commercial quantities, however, all isomers of heptafluoropropane are within the scope of the present invention.

5

The refrigerant fluids in Table 1 may be grouped into four categories, GROUP-A, GROUP-B, GROUP-C, and GROUP-D as set forth in Table 2. GROUP-A contains refrigerant fluids with the higher boiling points, GROUP-B contains refrigerant fluids that improve oil miscibility with mineral oils, tars and waxes. GROUP-C contains refrigerant fluids with the lowest boiling points. GROUP-D refrigerant fluids may be used to dilute the other three groups. Some refrigerant fluids (e.g. R-143a) may be in more than one GROUP. Flammability is listed as "very" for very flammable refrigerant fluids, "weak" for weakly or mildly flammable refrigerant fluids and "none" for nonflammable refrigerant fluids. The term "unkn" means "unknown".

10

15

Table 2

GROUP-A		GROUP-B		GROUP-C		GROUP-D	
Refrig	Flam	Refrig	Flam	Refrig	Flam	Refrig	Flam
R-227ea	none	R-F134	none	R-C216	none	R-134a	none
R-152a	weak	R-600a	very	R-125	none	R-1216	none
R-F218ca12	none	R-290	very	R-143a	weak	R-CF216	none
R-F143a	unkn	R-F143a	unkn	R-F125	none		
R-F227ca2	none	R-F170	very	R-218	none		
R-245cb	unkn	R-1270	very	R-32	weak		
R-134	none	R-600	very	R-116	none		
R-C318	none	R-C270	very	R-23	none		
R-CF216ca1	none			R-7146	none		
R-F218	none						

Preferred embodiments of the present invention include a mixture of refrigerant fluids with one or more components from GROUP-A, zero or more components from GROUP-B, one or more components from GROUP-C, and zero or more components from GROUP-D, subject to the three following conditions.

Condition 1. The resulting temperature versus pressure curve of a closed container containing said mixture of refrigerant fluids, such that all component refrigerant fluids coexist in both liquid and vapor states in the container, should approximate the temperature-pressure curve of a closed container of R-12 for the range of temperatures and pressures commonly used for R-134a refrigerant, about -40 degrees Fahrenheit to about 200 degrees Fahrenheit. The degree of approximation should be within about 15 percent to about 30 percent error. To account for the "glide" in the mixtures of refrigerant fluids, the "bubble point" pressure at a temperature

-12-

of 70 degrees Fahrenheit should be around 10 percent higher than the pressure (gauge pressure, PSIG) of R-134a. Increasing the mass fraction of components from GROUP-C and decreasing the mass fraction of components from GROUP-A will cause the pressure versus temperature curve of the mixture of refrigerant fluids to increase and vice versa. Rarely, two or more refrigerant fluids may be combined and the resultant boiling/bubble point of the mixture may not lie in between the boiling points of the components. This is the result of a partial or complete azeotrope formation. If an azeotrope is formed, the resultant boiling/bubble point is often near or a few degrees lower than the component with the lowest boiling point. If an unwanted azeotrope forms, additional components can be added to further modify the temperature-pressure curve.

In order to achieve good performance, it is usually necessary to have roughly equal liquid volumes of low (GROUP-C) and higher boiling components (GROUP-A) in the final mixture. This results in better utilization of the evaporator and condenser surface areas.

If the object is to produce a "high performance" or "higher capacity" mixture of refrigerant fluids, which may only be usable under certain conditions, such as automotive air conditioning, where extra horsepower is available for compressor operation, or in low temperature situations where the compressor is under loaded, then the mass fraction of the components from GROUP-C may be further increased about 5 to about 20 weight percent. Conversely, to produce a "reduced capacity" mixture of refrigerant fluids, the mass fraction of GROUP-C components may be reduced by about 5 to about 15 weight percent. Reduced capacity refrigerant mixtures will often perform poorly (but still useable) in "normal" systems. Air conditioning systems which were oversized when installed, may use a reduced capacity refrigerant to obtain a better equipment load match to the

heat load. Properly sized air conditioning systems provide far better humidity control (longer run times) than do oversized systems.

Condition 2. Optionally, about 0.5 to about 2 weight percent of GROUP-B components may be added to the mixture to prevent system clogging from solidified waxes and tars that may be present in a refrigeration system, especially if said system had been retrofitted to R-134a refrigerant from R-12 refrigerant. There is no need to be miscible with large amounts of mineral oils (as typically used in R-12 refrigeration systems), since the said systems will already contain oils which are miscible with R-134a and probably HFCs (hydrofluorocarbons) in general.

Condition 3. The resulting mixture of refrigerant fluids should be nonflammable or weakly flammable at worst. The maximum mass fraction of "very" flammable refrigerant fluid components will be limited to about 5 to about 10 percent. The maximum mass fraction of "weakly" flammable refrigerant fluid components will be limited to about 15 to about 60 percent. A test sample of the mixture of refrigerant fluids should be vapor leaked (fractionated) at several constant temperatures over the range of expected temperatures where the leaking may occur. Some temperatures for fractionation testing would typically be -20, 0, 40, 70, 120, 180 degrees Fahrenheit. Flammability tests should be conducted on the mass fractions of vapor and liquid phases and be analyzed with appropriate equipment (e.g. a gas chromatograph) at various points during each leak down to verify the mass fraction of flammable components does not become great enough to cause greater than "no" or "weak" flammability as desired. Flammability can also be reduced by placing the boiling point of a very or weakly flammable refrigerant fluid near a lesser flammable or nonflammable refrigerant fluid component with a similar boiling point. Total flammability may also be reduced by spreading out (by boiling point) the

flammable components over the entire mixture instead of using just one flammable component.

For the purposes of making the mixture of refrigerants of the preferred embodiments of the present invention, one needs to procure the following equipment, or equivalents. A mixing cylinder, which can be a  
5 standard refrigeration industry "recovery" cylinder, or a small propane (20 pounds net weight propane) tank is needed. These are U.S. Department of Transportation (DOT) rated at 240 PSIG or higher. This tank (or cylinder) must be clean. Also needed is a refrigeration (or equivalent) vacuum  
10 pump, scales, and a refrigeration manifold set (hoses and gauges).

The air must be removed from the mixing cylinder with a vacuum pump, such as any used by refrigeration service technicians. A deep vacuum gauge is needed to verify that about a 200 micron vacuum is achieved on the mixing cylinder. Deep vacuum gauges that read to less  
15 than 25 microns are commonly available at refrigeration supply houses.

This mixing cylinder is placed on electronic charging scales, of the type commonly available to the refrigeration service technician. These scales often read in 1/2 ounce increments up to a total of 60 pounds or more total weight.

20 A refrigerant mixture is made by connecting up each component supply cylinder to the mixing cylinder on scales, and weighing in the appropriate weight percentage of each component. The mixing hoses or manifolds should be purged or evacuated first to remove air and moisture. Each component supply cylinder should have a "dip tube" or eductor tube  
25 to withdraw the component in liquid phase. If the supply component cylinder does not have a dip tube, it must be inverted to obtain the component in liquid phase.



Although the components can be mixed in any order, it is easier to add the high boiling components first. The vacuum on the cylinder will usually be sufficient to draw in the required amount of the first component.

5 Some sort of liquid pump will be required to transfer the remaining GROUP-A and GROUP-B components as the pressure on the mixing cylinder will rise to match the supply cylinder.

10 Instead of a liquid pump, the mixing cylinder may be chilled by any convenient means to 10-20 degrees Fahrenheit colder than the supply cylinders. Alternately, the component supply cylinder may be heated to 10-20 degrees Fahrenheit warmer than the mixing cylinder to facilitate the transfer. A hot water bath or cylinder heating blanket works nicely for this purpose.

15 When transferring GROUP-C components, no pump will be needed, as the higher pressures of GROUP-C components will (rapidly) transfer them to the mixing cylinder. Caution is advised, for after the relatively slow transfers for GROUP-A and GROUP-B components into the mixing cylinder, GROUP-C components will transfer very quickly, possibly surprising the person doing the mixing, and causing too much of a component to be transferred.

20 A refrigerant mixture, just completed, should be allowed to thermally stabilize for 12 hours or more before temperature and pressure measurements are taken, if needed. If static pressure and temperature measurements are not needed, a mixture may be charged into a refrigeration or air conditioning system and operated without the 12 hour or  
25 more delay. A refrigerant mixture should always be unloaded from the mixing cylinder in liquid phase when charging into an appliance or other refrigeration system. This prevents fractionation from changing the

composition of the mixture during charging. The mixing cylinder may contain a "dip tube" to provide for unloading in liquid phase. If a mixing cylinder is used without a dip tube, the cylinder must be inverted to unload in liquid phase.

5           If a mixture contains significant mass fractions of components with high molecular mass, the molecular mass of the total refrigerant mixture will increase. This may be beneficial for operation in centrifugal chiller refrigeration systems.

10           The mixtures of refrigerants are zeotropic, which means the composition changes during evaporation and condensation phases of refrigeration or air conditioning system operation. Unlike a single component refrigerant, such as R-134a, zeotropic refrigerants do not evaporate or condense at a single temperature (for a given pressure), but they evaporate or condense over a small range or "glide" of temperatures.  
15           Depending on the temperature, the glides involved for the preferred embodiments of the present invention are in the order of 10 to 15 degrees Fahrenheit.

          Some refrigeration systems should see performance improvements upwards of about 30 to about 40 percent due to the glide factor, especially  
20           during the initial cool down period. Other systems will exhibit similar performance to that of R-134a. Events taking place in the condenser are broken down into 3 rough areas. The hot gas upon entering the condenser is first desuperheated, no condensation takes place in this area, just a relatively low amount of heat is rejected in cooling the hot gas down to the  
25           point where it is ready to condense. The second area involves the actual condensation of the gas, where a phase change occurs to liquid state. A relatively high amount of heat is given off due to the phase change.

Thirdly, the now liquid refrigerant is further cooled (called subcooling in the art), with a relatively low amount of heat rejected.

Zeotropic mixtures, such as those of the present invention, cause the condensation phase change area (and evaporation phase change area) to occupy more of the condenser (or evaporator), thus increasing the capacity of the condenser to reject or the evaporator to gain heat.

A stationary refrigeration system test stand was constructed from a conventional Copeland  $\frac{3}{4}$  horsepower, medium temperature, R-134a condensing unit, model FTAM-A075-IAA-201. The condensing unit consisted of a Copeland model RS54C1E-IAA-100 compressor, a small fan, a condenser, and a liquid receiver. The compressor was rated for 11.8 Amperes, 115 volts, 60 Hertz power. The compressor came factory charged with Polyol Ester (POE) oil, suitable for R-134a operation. The high side liquid line was connected to a Sporlan refrigeration drier, model C-053 followed by a liquid line sight glass. A Sporlan model BFF A C 43 FC ( $\frac{1}{2}$  - 1 ton) internally equalized expansion valve was used as the refrigerant metering device. The evaporator consisted of about 30 feet of  $\frac{3}{8}$  inch refrigeration copper wound into a coil of 20 turns of diameter about  $5 \frac{1}{2}$  inches and about  $11 \frac{1}{2}$  inches in height. The evaporator was connected back to the compressor via  $\frac{3}{8}$  inch tubing that contained an additional sight glass to monitor any liquid refrigerant that might be returning to the compressor.

The evaporator coil was aligned with its axis vertical and immersed in a Rubbermaid two gallon insulated thermal jug, filled with about  $1 \frac{7}{8}$  gallons (14.42 pounds) of distilled water. The test runs were all made under the same starting conditions: 75 degrees Fahrenheit condenser inlet air and the water was at 66 degrees Fahrenheit. The expansion valve was adjusted (visually) for about 0 degrees of suction line superheat (at the

point of no liquid refrigerant returning to the compressor as monitored through the sight glass). R-134a was used as the baseline (control) refrigerant. Three degrees of condenser airflow restrictions were employed to simulate "dirt" buildup encountered in normal long term operation. The first degree was no airflow restriction, the second degree was about a 50% reduction in airflow accomplished by placing two pieces of porous ½ inch thick foam rubber over the air inlet side of the condenser. The third degree of reduction was achieved by taping cardboard to the air inlet side of the condenser, covering about ¾ (top) of it's area. The bottom ¼ was covered with the same foam as used to provide the second degree of restriction. About 90% of the airflow was blocked by the third degree of restriction. This is a highly abnormal condition (90% reduction) and probably will not occur often in practice. On the other hand, a 50% reduction in air flow could be expected to occur often in practice from dirt buildup. It was noted that the condenser on this R-134a condensing unit was sized about 50% larger than a condenser on the same capacity R-12 condensing unit. Thermocouples were attached to the compressor hot gas discharge line, and to the condenser liquid line out. Condenser outlet air, compressor current draw, and system low side and high side pressures were monitored at 1, 5, 10, 15, and 20 minutes after startup. At the 20 minute mark, the system was shut down, and the thermal jug on the evaporator was removed and weighed. Ice which was made during the run remained on the evaporator coils. The amount of ice made was determined by weighing the remaining water after each run.

The energy use was computed by doing a simple integration of the compressor amp draw. The average amp draw was used from each segment of the run to determine the energy use of that segment. For example, to compute the energy use for the first segment (minute 1 through minute 5), the amp draw at one minute was averaged with the amp

draw at 5 minutes. The average amp draw was multiplied by 115 (volts) to obtain the average power for the segment and multiplied by the time used (in hours) to obtain the power (watt-hours) used for the segment. The energy used for a given run was the sum of the energy used in each of the four segments. Data (including amp draw) from minute 0 to minute 1 was ignored in each run, to allow the system to reach stability. The heat removed to cool down the 1.7 gallons of water from 66 degrees Fahrenheit to 32 degrees Fahrenheit, along with the evaporator coils, and the inside of the thermal jug is not accounted for in the amount of ice made, but it was the same for each run. Results are summarized in Table 3, below.

Table 3.

Refrig.	ICE MADE (in pounds)			Total Watt-hours used			Watt-hours / lb of ice		
	NONE	PARTIAL	VERY	NONE	PARTIAL	VERY	NONE	PARTIAL	VERY
R-134a	5.055	4.695	3.915	429.24	434.32	445.24	84.91	92.51	113.73
Ex. 1	5.225	4.740	3.735	422.72	430.96	428.38	80.90	90.92	114.69
Ex. 2	4.840		4.385	423.68		423.68	86.59		96.62

Each refrigerant was tested with the condenser unrestricted (labeled NONE), the condenser partially restricted for about a 50% reduction in airflow (labeled PARTIAL), and very restricted for about a 90% reduction in air flow (labeled VERY).

Example 1

Three pounds of R-227ea/152a/125 55/5/40, a "drop-in" substitute refrigerant mixture for an R-134a stationary refrigeration system were created in the manner set forth above. Although the temperature-pressure curve is a little higher than optimal, it performed well when charged into the test stand described above. The higher than normal temperature-pressure curve resulted from the necessity of having roughly equal liquid volume

portions of the low and high boiling components. The refrigerant mixture of this example produced 3.4% more ice than R-134a while using 1.5% less energy for the case of unrestricted condenser airflow. For the partially blocked condenser (about 50% airflow reduction), this mixture still made  
5 1% more ice than R-134a while using 0.8% less energy.

For the highly obstructed condenser (about 90% airflow reduction) case, R-134a fared better. R-134a produced 4.8% more ice than the mixture of this example, but R-134a also used 3.9% more energy. The extremely obstructed condenser is not often encountered in the field, as  
10 the system would most likely have failed before this state was reached.

### Example 2

Three pounds of R-227ea/152a/125 60/5/35, a "drop-in" substitute refrigerant mixture for an R-134a stationary refrigeration system were created in the manner set forth above. Although the temperature-pressure  
15 curve is a little higher than optimal, but closer to R-134a than the mixture of Example 1, it only produced more ice than R-134a in the case of the highly obstructed condenser (producing 12% more ice and using 4.8% less energy). R-134a outperformed the mixture of this example when the condenser was unrestricted. R-134a made 4.4% more ice while using  
20 1.3% more energy. This mixture would be useful for continuous operation in high ambient temperatures and/or heavy dirt fouling of the condenser airflow (or water flow if water cooled).

### Example 3

3.2 pounds of the mixture of Example 1, a "drop-in" substitute  
25 refrigerant mixture for an R-134a automotive air conditioning system were created in the manner set forth above. 2.9 pounds of this mixture were charged into 1982 Chevy pickup truck air conditioning system. This

-21-

system, based on the GM "R4" compressor, was originally designed for R-12 refrigerant, and had been retrofitted to R-134a during the previous year. Retrofitting including replacing the condenser with a larger one, and adding a second outboard condenser fan to provide more condenser airflow and changing the oil from mineral oil to PAG oil. The R-134a retrofit had performed poorer cooling (truck is owned by a Lafayette, Indiana, air conditioning service shop and the R-134a retrofit was a "test" retrofit) than did the original R-12, even after numerous attempts at "tweaking" its performance on R-134a. When operated with the mixture of this example, (ambient temperature was 81 degrees Fahrenheit), excellent cooling performance was obtained, although the head pressure was a little higher than normal, but still well within system design limits. The air conditioner controls were set on "MAX" (highest fan speed, recirculate). The low pressure cutout switch was set at (the standard setting) of 24 PSIG. The second condenser fan, added during the R-134a retrofit, was disconnected for this example, creating a tougher test.

Driving Conditions	Suction pressure (PSIG)	Head pressure (PSIG)	Duct Temperature (degrees Fahrenheit)
5 Not moving, engine idle	55	235	52
In town, 35 MPH	32	220	42
Highway, 55 MPH	25	190	39
Highway, 65 MPH	24	175	38

10 The owner of the truck in this example stated that the cooling performance of the mixture of this example significantly exceeded the cooling performance of R-134a, and somewhat exceeded the cooling performance of the original R-12 system.

#### Example 4

15 25 pounds of the mixture of Example 1, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system, were created in the manner set forth above. A 199X Cadillac vehicle, that was manufactured with a R-134a air conditioning system, had the original R-134a charge removed and was evacuated and recharged with 2 pounds of the mixture of this example. Head pressures ran about 10% higher than  
20 with R-134a, suction pressures were the same. Cooling performance (82 degrees Fahrenheit) was superior to the cooling performance of the original R-134a. Duct temperatures (MAX Fan, recirculate) were about 5



degrees Fahrenheit colder at idle and 10 to 14 degrees colder when doing normal "in town" driving. This vehicle was taken to Florida (winter), and has been performing well for four months in 80 to 90 degree Fahrenheit ambient conditions.

5

#### Example 5

3.2 pounds of R-227ea/152a/125 62/8/30, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system were created in the manner set forth above. All of this mixture was charged into the air conditioning system of the vehicle in Example 3. Ambient  
10 temperature was 87 degrees Fahrenheit. While driving 55MPH, the charge was adjusted by admitting liquid refrigerant back into the (metered) charging cylinder. Optimum performance was obtained with a system charge of 2.9 pounds. Performance similar to R-12 was obtained. Highway driving (55 MPH) produced duct temperatures of 42 degrees  
15 Fahrenheit on MAX fan speed (recirculate), and 39 degrees Fahrenheit on one fan speed slower. The head pressure ranged from 250 PSIG at idle down to 175 PSIG while driving 55 MPH. Although the cooling performance of this example's refrigerant mixture was not as good as Example 3 refrigerant mixture, it was none the less "acceptable", and  
20 comparable to R-12, which was somewhat better than R-134a would have been.

#### Example 6

25 25 pounds of R-227ea/125 75/25, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system were created in the manner set forth above. 3.2 pounds of this mixture were charged into the air conditioning system of the vehicle in Example 3. Air conditioner controls were set at MAX fan (recirculate). Ambient temperature was 78

-24-

degrees Fahrenheit. Head pressure was 200 PSIG at idle, which dropped to 130 PSIG at 30 MPH driving speeds. This is too much of a drop for the head pressure, and could cause refrigerant starvation in the evaporator. At idle, not moving, the suction pressure was 40 PSIG, which dropped to 24 PSIG at 30 MPH driving, causing the low pressure cutout switch to open, causing the compressor to cycle off. The cold air duct temperature at this point was about 42 degrees Fahrenheit. Later in the day, the ambient temperature warmed up 85 degrees Fahrenheit. Head pressure at idle was still about 200 PSIG, and the 30 MPH driving head pressure rose to 150 PSIG. Duct temperature remained the same at 42 degrees Fahrenheit; but the higher head pressure caused more refrigerant to be admitted to the evaporator resulting in a faster cool down compared to 78 degree Fahrenheit temperatures earlier in the day.

#### Example 7

R-600a/227ea/125 1/75/24, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system, is created in the manner set forth above. The mixture of this Example shows good results in computer simulation with NIST program REFPROP V5.10. The glide calculates to be 17.5 degrees Fahrenheit (bubble point - dew point) at 70 degrees Fahrenheit ambient. The glide is a little bit too high. The R-600a component keeps waxes and tars dissolved, if present.

#### Example 8

R-600a/227ea/125/134a 1/67/22/10, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system, is created in the manner set forth above. The mixture of this Example shows good results in computer simulation with NIST program REFPROP V5.10.

The glide calculates to be 15.8 degrees Fahrenheit at 70 degrees Fahrenheit ambient, which is about right. R-134a is used to "dilute" the glide. Tars and waxes are dissolved by the R-600a component in the mixture.

5

#### Example 9

R-245cb/125/290 58/41/1, a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system, is created in the manner set forth above. The mixture of this Example shows good results in computer simulation with NIST program REFPROP V5.10. The glide  
10 calculates to be 19.5 degrees Fahrenheit at 70 degrees Fahrenheit ambient, which is too high, but usable. Protection from plugging from tars and waxes is provided by the R-290 component.

#### Example 10

R-245cb/125/290/134a 59/20/1/20, a "drop-in" substitute  
15 refrigerant mixture for an R-134a automotive air conditioning system, is created in the manner set forth above. The mixture of this Example shows good results in computer simulation with NIST program REFPROP V5.10. The glide calculates to be 16 degrees Fahrenheit at 70 degrees Fahrenheit ambient, which is about right. R-134a is used to "dilute" the glide. Tars and  
20 waxes are dissolved by the R-290 component of the mixture.

#### Example 11

R-134/143a/290 78/21/1 (note: R-134, not R-134a), a "drop-in" substitute refrigerant mixture for an R-134a automotive air conditioning system, is created in the manner set forth above. The mixture of this  
25 Example showed good results in computer simulation with NIST program REFPROP V5.10. The glide calculates to be 14 degrees Fahrenheit at 70

degrees Fahrenheit ambient, which is about right. Tars and waxes are dissolved by the R-290 component in the mixture. The critical temperature of this mixture is calculated to be around 240 degrees Fahrenheit, which is excellent.

5

#### Examples 12 - 24

Most of the "drop-in" substitute refrigerant mixtures for R-134a of Examples 12 - 24, which are tabulated in Table 4, show good results in computer simulated with NIST program REFPROP V5.10. The refrigerant mixtures of Examples 1 - 15 are also included in Table 4 for completeness.

10

General comment(s) are included for most entries in Table 4. The "Fig." column refers to which Figure of FIGS. 1 - 8 contains the temperature-pressure chart for the Example mixture. The "Crit" column refers to the estimated critical temperature calculated from computer program REFPROP V5.10.

Table 4

Ex	Components	Composition	Crit	Fig	General comments(all glides at 70°F)
1	R-227ea/152a/125	55/5/40	207	1	
2	R-227ea/152a/125	60/5/35	210	1	
3	Same as Example 1				
4	Same as Example 1				
5	R-227ea/152a/125	62/8/30	215	2	
6	R-227ea/125	75/25	214	2	
7	R-600a/227ea/125	1/75/24	214		glide a little high (17.5° F)
8	R-600a/227ea/125/134a	1/67/22/10	216	3	good glide (15.8° F)
9	R-245cb/125/290	58/41/1	210	3	glide a little high (19.5° F)
10	R-245cb/125/290/134a	59/20/1/20	223	4	good glide (16° F)
11	R-134/143a/290	78/21/1	240	4	good glide (14° F), good crit temp
12	R-227ea/143a/290	82/17/1	215	5	glide a little high (18.5° F)
13	R-245cb/143a/600	73/26/1	221	5	glide OK (17.1° F)
14	R-245cb/E125/600	65/34/1			
15	R-E143a/E125/600	90/9/1			
16	R-227ea/152a/125/600	61/15/23/1	222	6	glide a little low (13.4° F)
17	R-600a/227ea/125/134a	1/57/32/10	209	6	High performance version of Ex8
18	R-245cb/125/290	48/51/1	203	7	High performance version of Ex9
19	R-245cb/125	58/42	210		Ex9 without an oil miscibility improver
20	R-227ea/143a	82/18	215		Ex12 without an oil miscibility improver
21	R-245cb/143a	73/27	221		Ex13 without an oil miscibility improver
22	R-227ea/152a/125	50/10/40	210	7	higher crit temp, lower glide than Ex1
23	R-227ea/152a/125	45/15/40	213		higher crit temp, lower glide than Ex1
24	R-227ea/152a/125	45/20/35	218		higher crit temp, lower glide than Ex1

There exist thousands of possible combinations and permutations from the refrigerant fluids listed in Table 1 that could produce a refrigerant substitute for R-134a. Many combinations can be ruled out under conditions 1,2, and 3 listed above. Other combinations may still provide a good refrigerant, but may not be currently environmentally acceptable, but they may become acceptable in the future as new evidence and understanding of the environment proceeds. Other combinations from Table 1 may produce R-134a "drop-in" substitutes that have low critical temperatures, below about 215 degrees Fahrenheit, and still provide satisfactory performance in the majority of climates, but prove unsatisfactory in extreme heat or very high humidity climates.

For any given combination of components from Table 1, above, that produce a useable "drop-in" substitute for R-134a, many permutations (ranges) of each component's weight percentage are possible. GROUP-C components (see discussion in Condition 1, above), may be varied over the range of about -10 to +15 weight percent from their "normal centerline" values used to create a normal temperature-pressure curve. This allows for special uses such as "low capacity" and "high capacity" refrigerant mixtures. Adjustment of weight percentages of GROUP-C components, must be accompanied by a corresponding opposite adjustment in GROUP-A components so that the total of all weight percentages remains at 100 percent.

I claim:

1. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 39 – 77 weight percent:  
5 heptafluoropropane, about 2 - 25 weight percent 1,1-difluoroethane, and about 23 – 47 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.
2. The mixture of refrigerants of claim 1 in which  
10 heptafluoropropane is present in about 55 weight percent, 1,1-difluoroethane is present in about 5 weight percent, and pentafluoroethane is present in about 40 weight percent.
3. The mixture of refrigerants of claim 1 in which  
15 heptafluoropropane is present in about 60 weight percent, 1,1-difluoroethane is present in about 5 weight percent, and pentafluoroethane is present in about 35 weight percent.
4. The mixture of refrigerants of claim 1 in which  
20 heptafluoropropane is present in about 62 weight percent, 1,1-difluoroethane is present in about 5 weight percent, and pentafluoroethane is present in about 30 weight percent.
5. The mixture of refrigerants of claim 1 in which  
heptafluoropropane is present in about 50 weight percent, 1,1-difluoroethane is present in about 10 weight percent, and pentafluoroethane is present in about 40 weight percent.

6. The mixture of refrigerants of claim 1 in which heptafluoropropane is present in about 45 weight percent, 1,1-difluoroethane is present in about 15 weight percent, and pentafluoroethane is present in about 40 weight percent.

5 7. The mixture of refrigerants of claim 1 in which heptafluoropropane is present in about 45 weight percent, 1,1-difluoroethane is present in about 20 weight percent, and pentafluoroethane is present in about 35 weight percent.

10 8. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 75 weight percent heptafluoropropane, and about 25 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

15 9. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 1 weight percent isobutane, about 75 weight percent heptafluoropropane, and about 24 weight percent pentafluoroethane, with the weight percentages of said components being  
20 weight percentages of the overall mixture.

10. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 1 weight percent isobutane, about 22 - 57 weight percent heptafluoropentane, about 22 - 32 weight percent



pentafluoroethane, and about 10 weight percent 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

11. The mixture of refrigerants of claim 10 in which isobutane is present in about 1 weight percent, heptafluoropentane is present in about 67 weight percent, pentafluoroethane is present in about 22 weight percent, and 1,1,1,2-tetrafluoroethane is present in about 10 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

12. The mixture of refrigerants of claim 10 in which isobutane is present in about 1 weight percent, heptafluoropentane is present in about 57 weight percent, pentafluoroethane is present in about 32 weight percent, and 1,1,1,2-tetrafluoroethane is present in about 10 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

13. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 48 - 58 weight percent 1,1,1,2,2-pentafluoropropane, about 41 - 51 weight percent pentafluoroethane, and about 1 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

14. The mixture of refrigerants of claim 13 in which 1,1,1,2,2-pentafluoropropane is present in about 58 weight percent, pentafluoroethane is present in about 41 weight percent, and propane is

present in about 1 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

15        15.    The mixture of refrigerants of claim 13 in which 1,1,1,2,2-pentafluoropropane is present in about 48 weight percent, pentafluoroethane is present in about 51 weight percent, and propane is present in about 1 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

10        16.    A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 59 weight percent 1,1,1,2,2-pentafluoropropane, about 20 weight percent pentafluoroethane, about 1 weight percent propane, and about 20 weight percent 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

15        17.    A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 58 weight percent 1,1,1,2,2-pentafluoropropane and about 42 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

20

18.    A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 78 weight percent 1,1,2,2-tetrafluoroethane, about 21 weight percent 1,1,1-trifluoroethane, and about

1 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

19. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 82 weight percent  
5 heptafluoropropane, about 17 weight percent 1,1,1-trifluoroethane, and about 1 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

20. A mixture of refrigerants that is a drop-in substitute for  
10 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 82 weight percent heptafluoropropane, and about 18 weight percent 1,1,1-trifluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

15 21. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 73 weight percent 1,1,1,2,2-pentafluoropropane, about 26 weight percent 1,1,1-trifluoroethane, and about 1 weight percent n-butane, with the weight percentages of said  
20 components being weight percentages of the overall mixture.

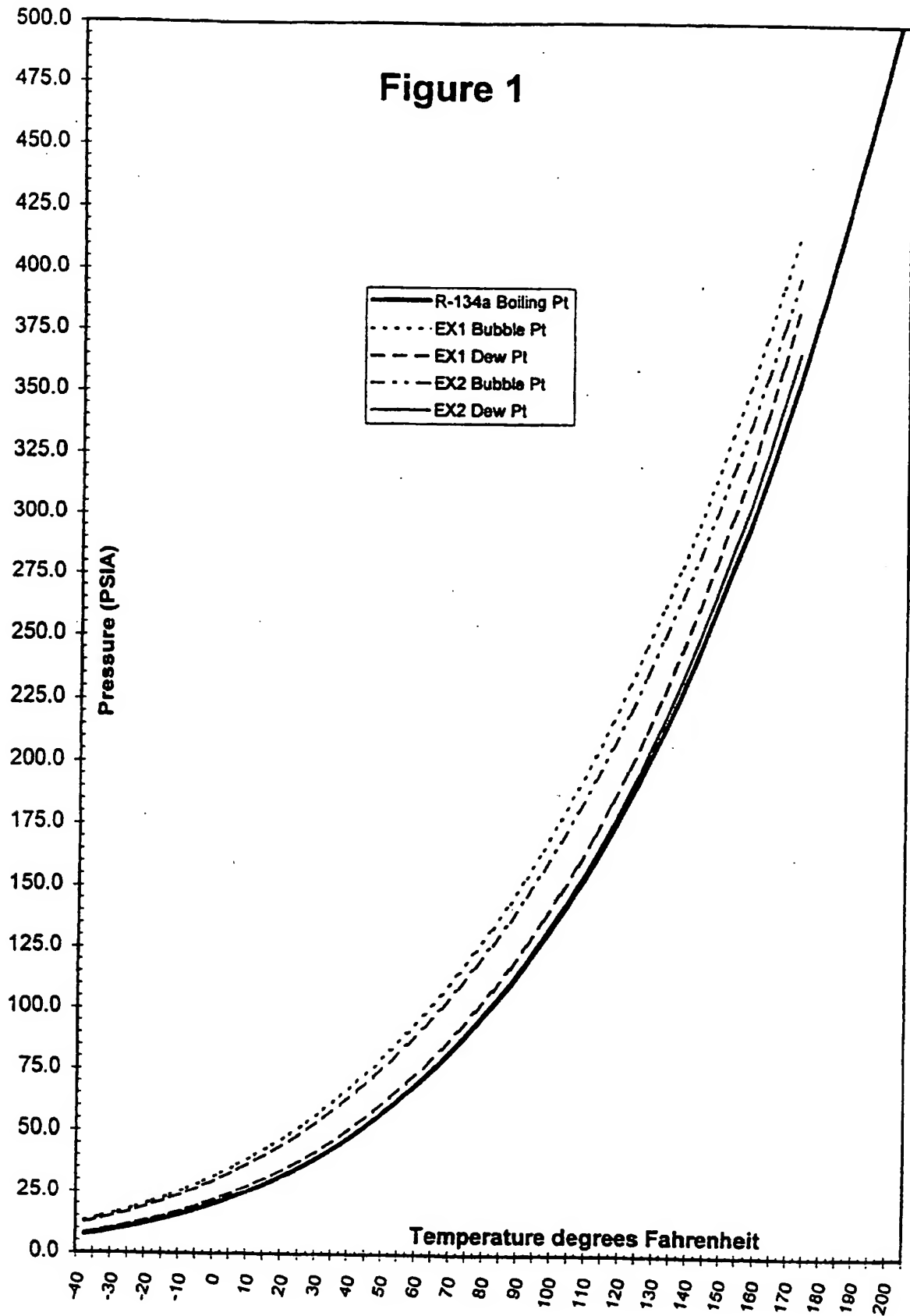
22. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 73 weight percent 1,1,1,2,2-pentafluoropropane, about 27 weight percent 1,1,1-trifluoroethane, with the

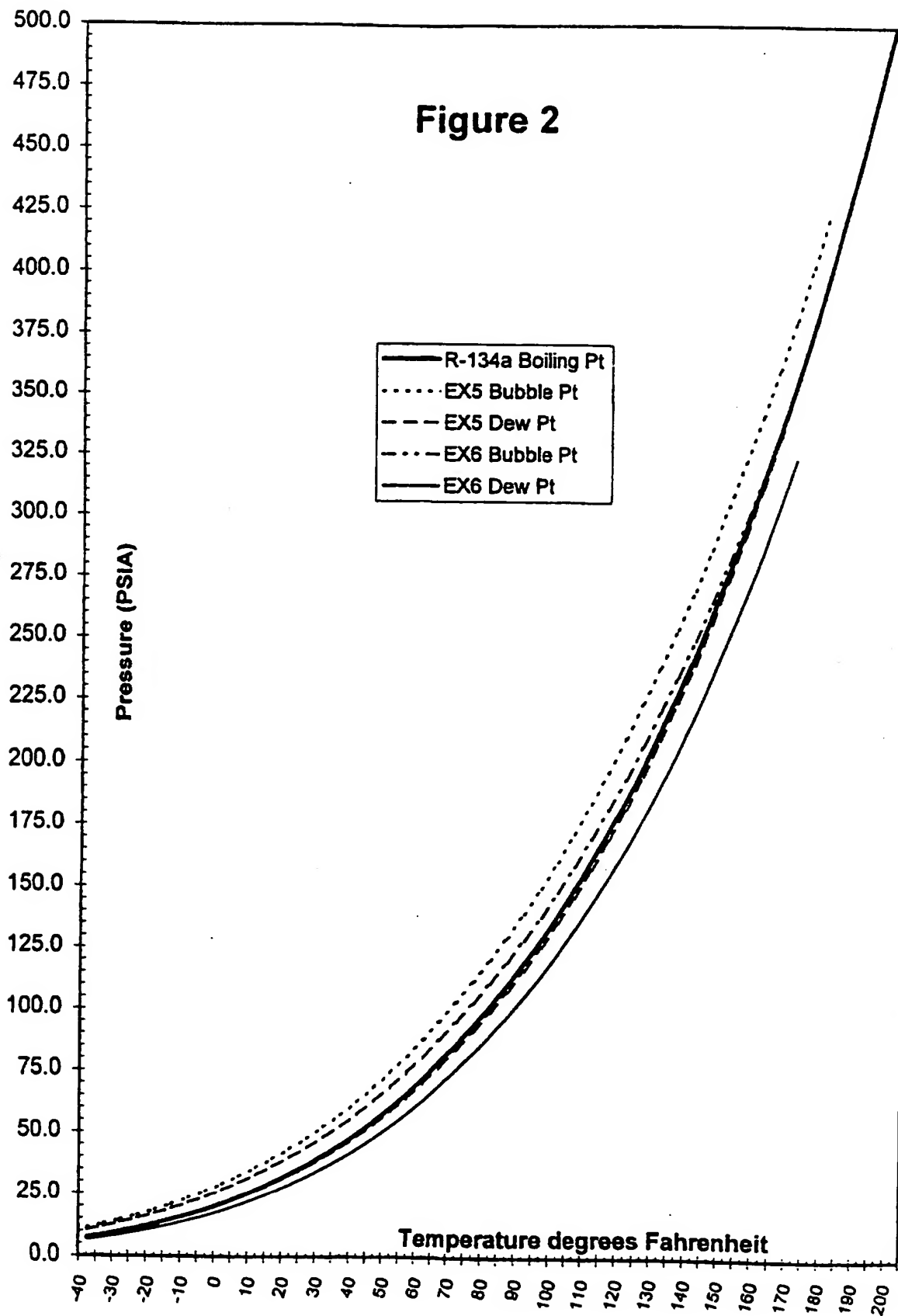
weight percentages of said components being weight percentages of the overall mixture.

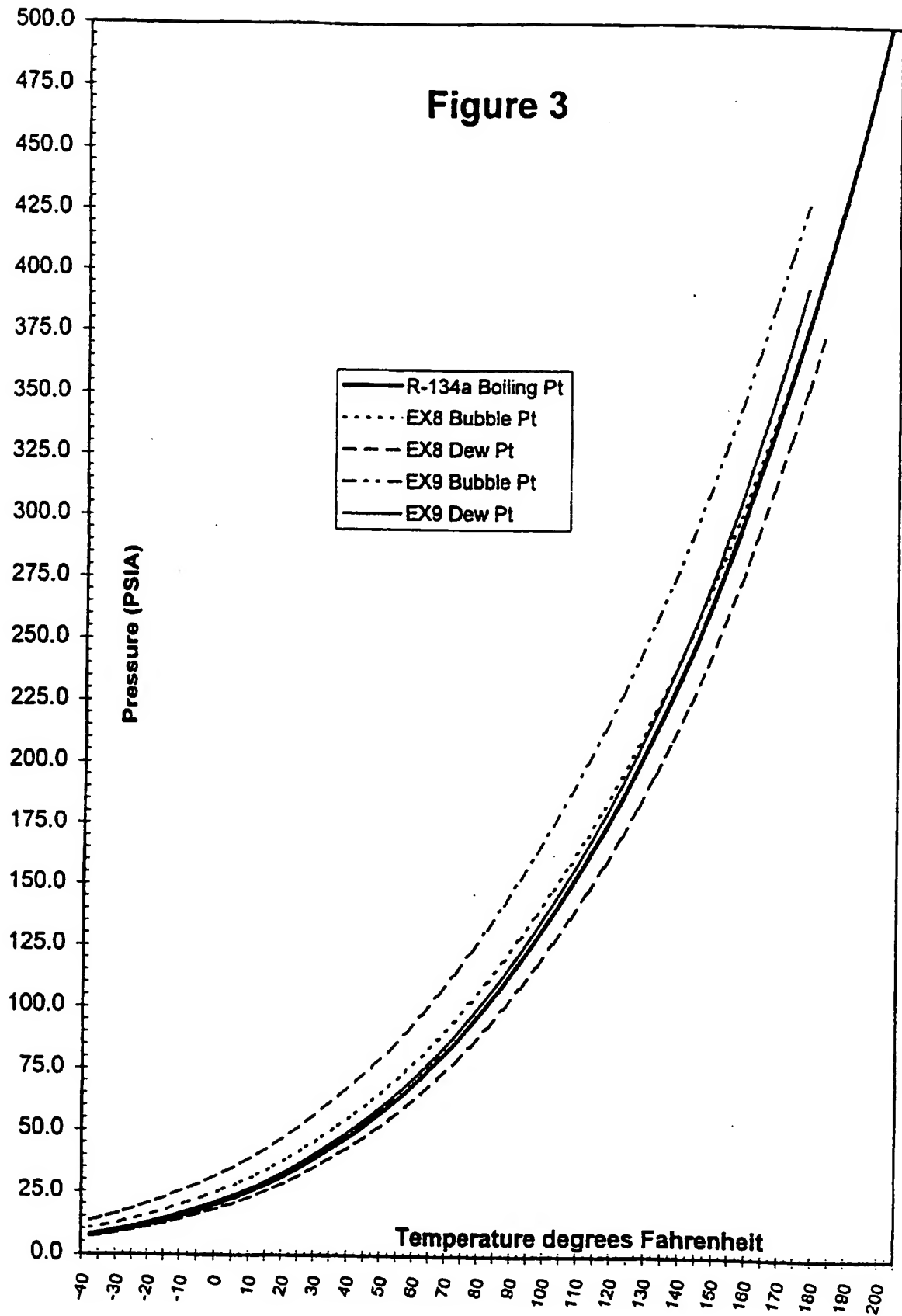
23. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 65 weight percent 1,1,1,2,2-pentafluoropropane, about 34 weight percent difluoromethyltrifluoromethyl ether, and about 1 weight percent n-butane, with the weight percentages of said components being weight percentages of the overall mixture.

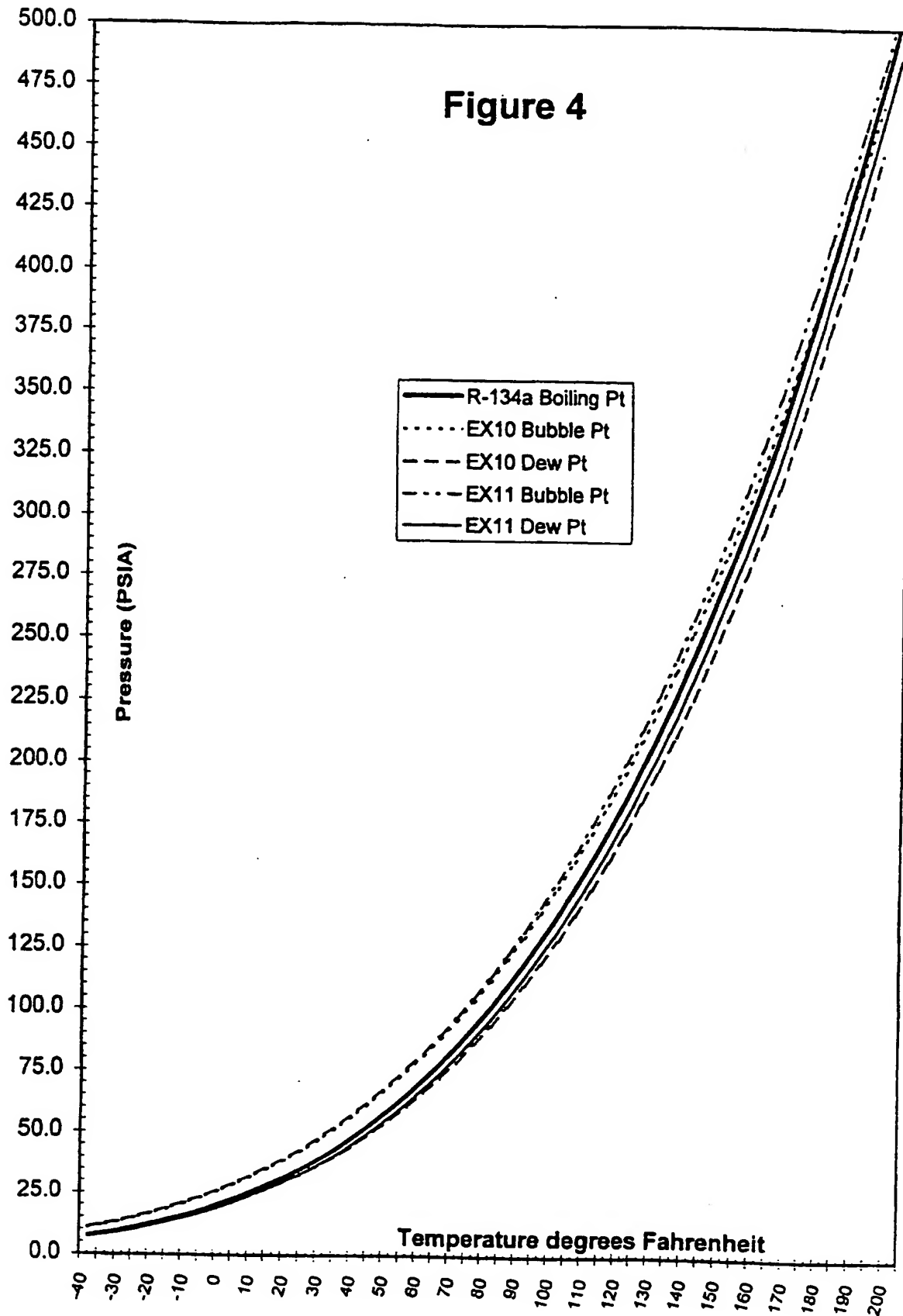
24. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 90 weight percent methyl trifluoromethyl ether, about 9 weight percent difluoromethyltrifluoromethyl ether, and about 1 weight percent n-butane, with the weight percentages of said components being weight percentages of the overall mixture.

25. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 61 weight percent heptafluoropropane, about 15 weight percent 1,1-difluoroethane, about 23 weight percent pentafluoroethane, and about 1 weight percent n-butane, with the weight percentages of said components being weight percentages of the overall mixture.

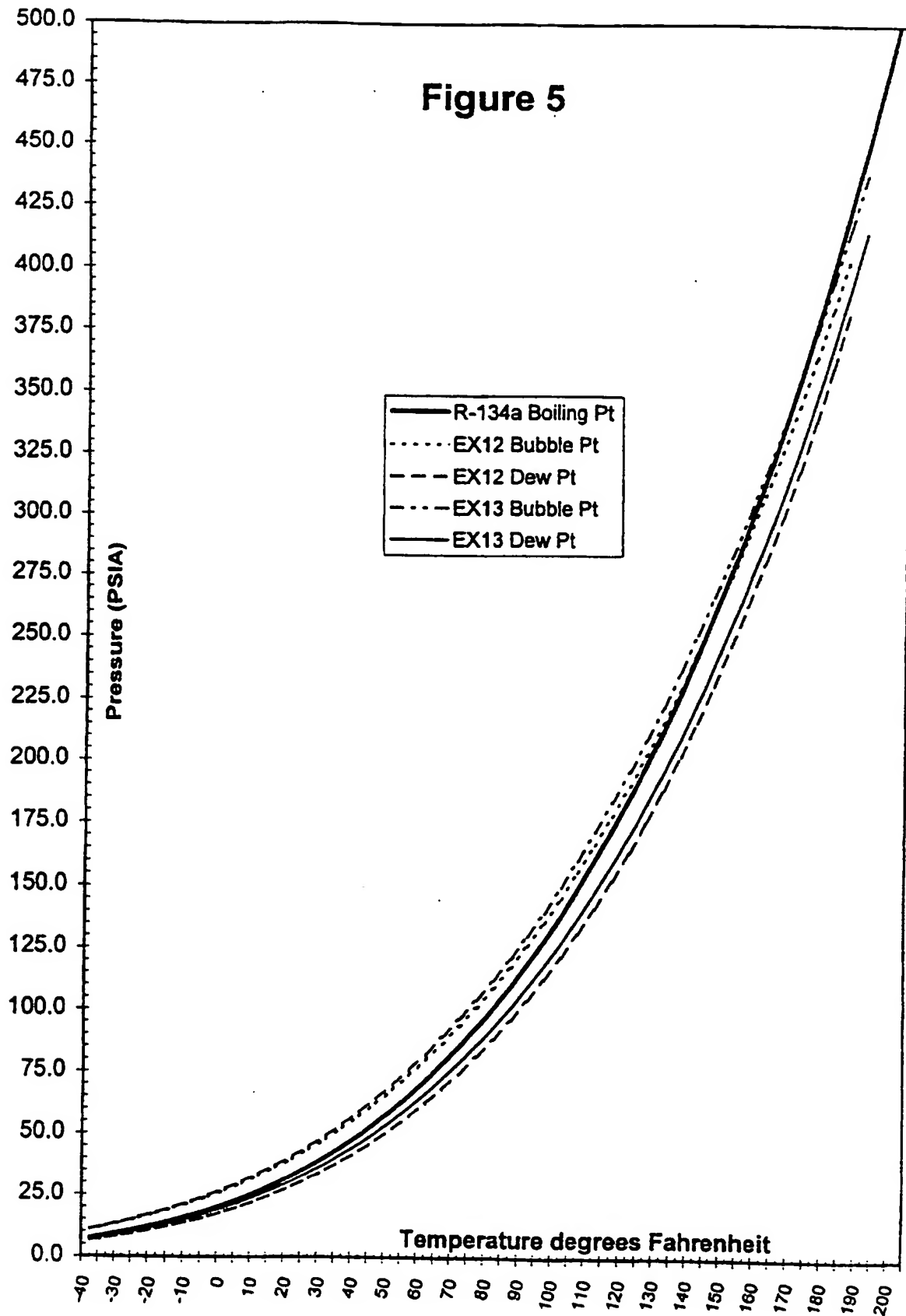


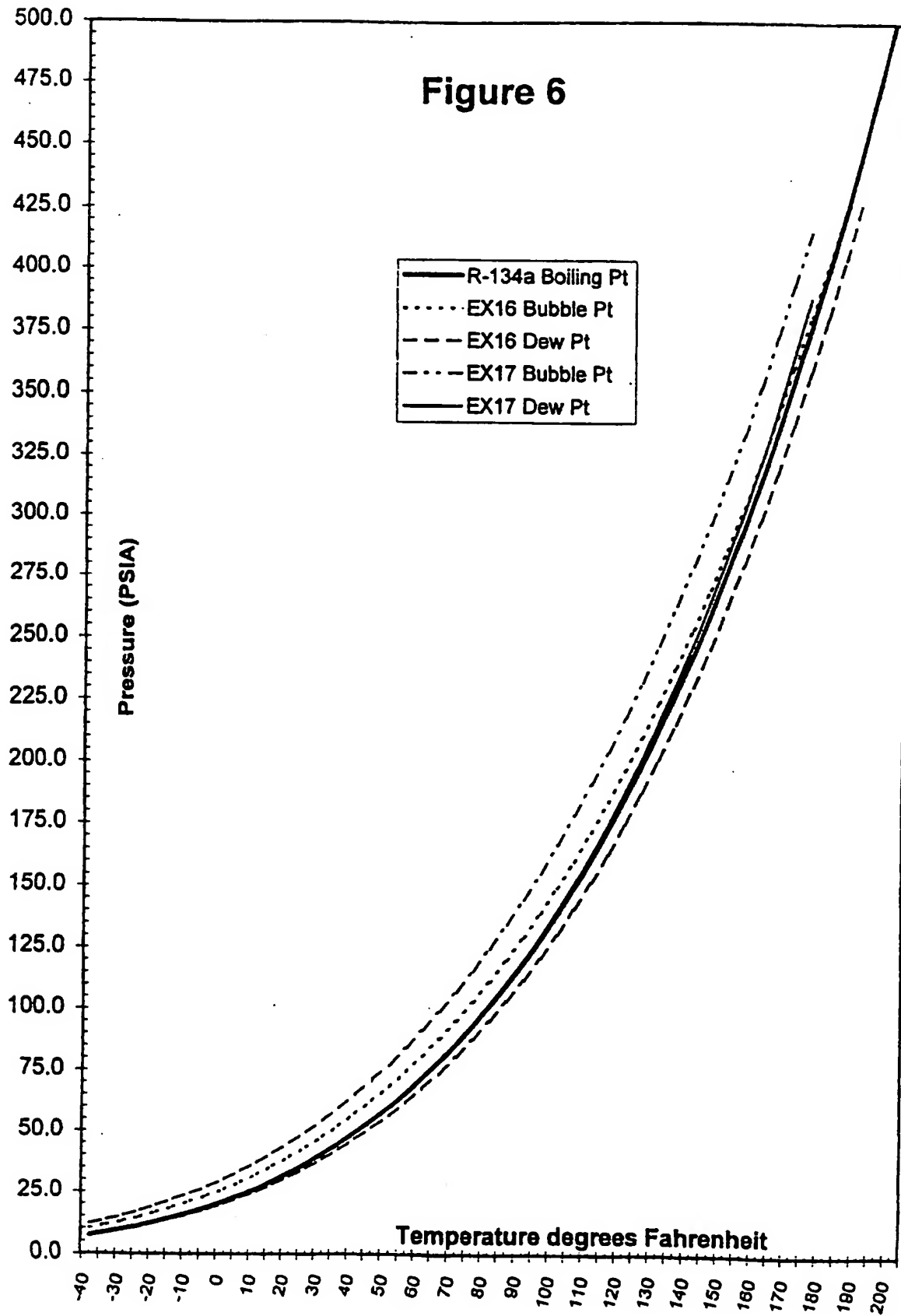


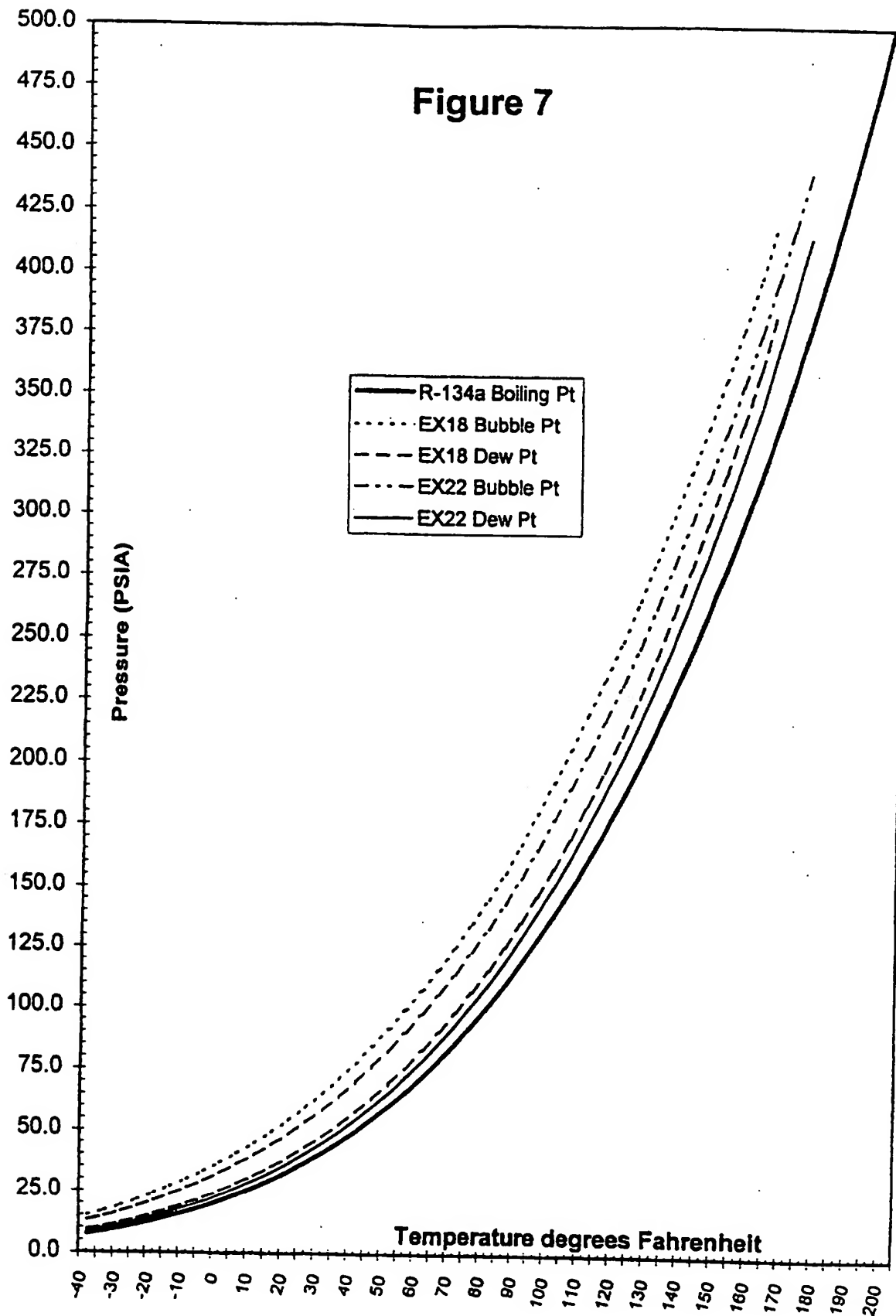


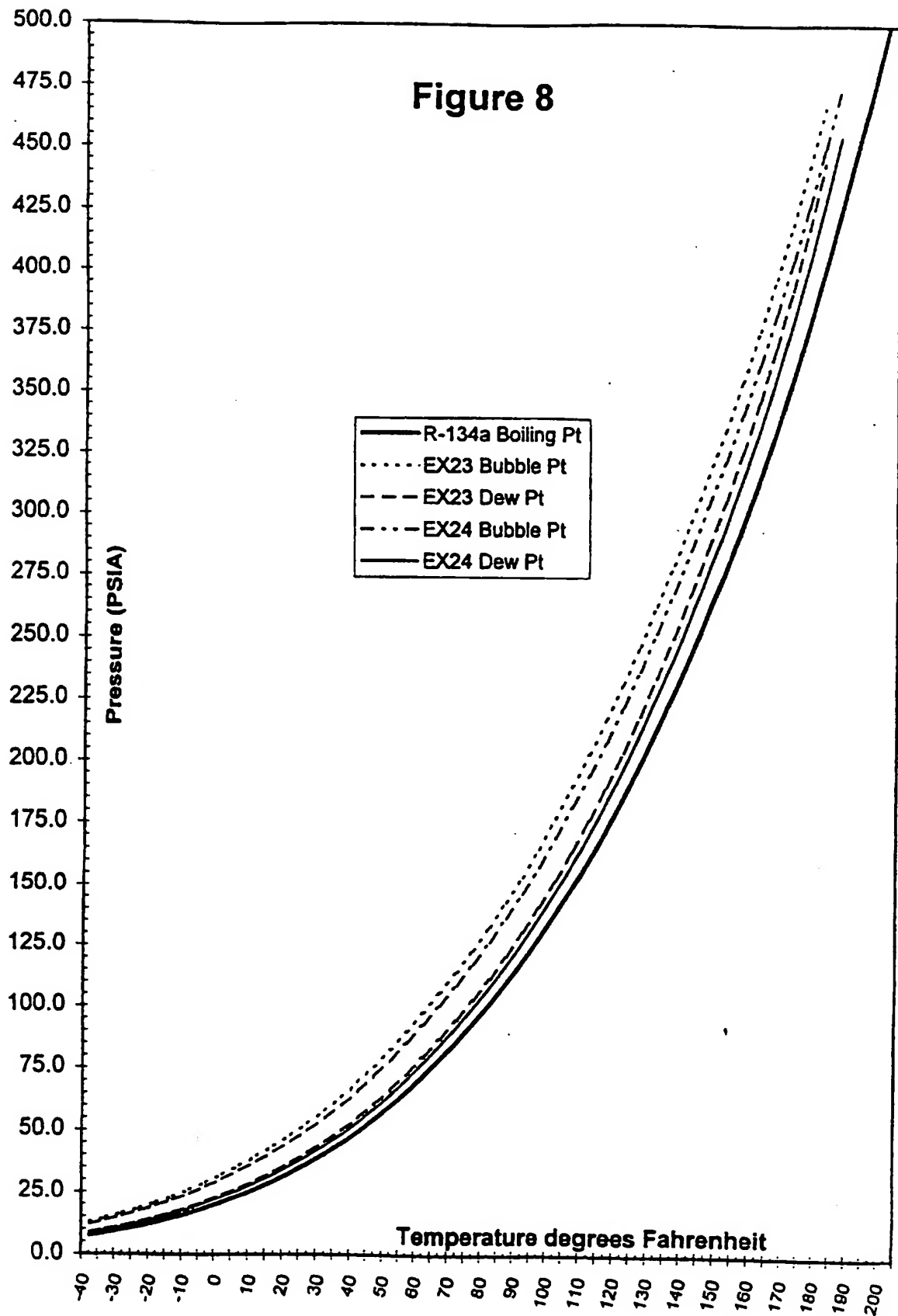












## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/04592

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C09K 5/04

US CL : 252/67; 62/114

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/67; 62/114

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE, DIALOG

search terms, heptafluoropropane, difluoroethane, pentafluoroethane, pentafluoropropane, propane

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94/00529 A1 (GREAT LAKES CHEMICAL CORPORATION) 06 January 1994, Abstract, page 6, lines 16-18, Example 1 (page 8).	1-7
Y	WO 93/05105 A1 (DAIKIN INDUSTRIES, LTD.) 18 March 1993, Abstract, page 31, lines 5-10.	1-7
Y	EP 0451692 A2 (DAIKIN INDUSTRIES, LIMITED) 16 October 1991, Abstract, page 3, lines 1-25.	1-7
Y	JP 3-093,890 A (DAIKIN KOGYO KK) 18 April 1991, claim 1, page 3 of the translation.	1-7
Y	WO 92/16597 A1 (ALLIED-SIGNAL INC.) 01 October 1992, page 5, line 9 - page 6, line 20.	13-15

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be of particular relevance	* X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &*	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

02 JULY 1997

Date of mailing of the international search report

01 AUG 1997

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

CHRISTINE SKANE

Telephone No. 703-308-2526

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/04592

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 93/11201 A1 (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY) 10 June 1993, claim 61 (page 38), page 4, lines 24-29.	13-15

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/04592

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  
1-7 and 13-15
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/04592

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-7, drawn to a mixture of refrigerants comprising heptafluoropropane, 1,1-difluoroethane and pentafluoroethane.

Group II, claim(s) 8, drawn to a mixture of refrigerants comprising heptafluoropropane and pentafluoroethane.

Group III, claim(s) 9, drawn to a mixture of refrigerants comprising isobutane, heptafluoropropane and pentafluoropropane.

Group IV, claim(s) 10-12, drawn to a mixture of refrigerants comprising isobutane, heptafluoropentane, pentafluoroethane and 1,1,1,2-tetrafluoroethane.

Group V, claim(s) 13-15, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane, pentafluoroethane and propane.

Group VI, claim(s) 16, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane, pentafluoroethane, propane and 1,1,1,2-tetrafluoroethane.

Group VII, claim(s) 17, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane and pentafluoroethane.

Group VIII, claim(s) 18, drawn to a mixture of refrigerants comprising 1,1,2,2-tetrafluoroethane, 1,1,1-trifluoroethane and propane.

Group IX, claim(s) 19, drawn to a mixture of refrigerants comprising heptafluoropropane, 1,1,1-trifluoroethane and propane.

Group X, claim(s) 20, drawn to a mixture of refrigerants comprising heptafluoropropane and 1,1,1-trifluoroethane.

Group XI, claim(s) 21, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane, 1,1,1-trifluoroethane and n-butane.

Group XII, claim(s) 22, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane and 1,1,1-trifluoroethane.

Group XIII, claim(s) 23, drawn to a mixture of refrigerants comprising 1,1,1,2,2-pentafluoropropane, difluoromethyltrifluoromethyl ether and n-butane.

Group XIV, claim(s) 24, drawn to a mixture of refrigerants comprising methyl trifluoromethyl ether, difluoromethyltrifluoromethyl ether and n-butane.

Group XV, claim 25, drawn to a mixture of refrigerants comprising heptafluoropropane, 1,1-difluoroethane, pentafluoroethane and n-butane.

The inventions listed as Groups I-XV do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The present claims set forth various combinations of individual refrigerants, wherein some of the claims contain no common components. Inasmuch as the various components would have different effects within the mixtures, there is no commonality of a special technical feature other than that each composition is useable as a refrigerant. However, this is a use of the composition, and not the composition per se.



(51) International Patent Classification <sup>6</sup> : C09K 5/04		A1	(11) International Publication Number: WO 97/34961
			(43) International Publication Date: 25 September 1997 (25.09.97)
(21) International Application Number: PCT/US97/04592		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, TT, UA, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 21 March 1997 (21.03.97)			
(30) Priority Data: 60/013,946 22 March 1996 (22.03.96) US			
(71)(72) Applicant and Inventor: GOBLE, George, H. [US/US]; 286 West Navajo, West Lafayette, IN 47906 (US).			
(74) Agents: BROWNING, Clifford, W. et al.; Woodard, Emhardt, Naughton, Moriarty & McNett, Bank One Center/Tower, Suite 3700, 111 Monument Circle, Indianapolis, IN 46204 (US).		<p><b>Published</b></p> <p><i>With international search report.</i></p> <p><i>With amended claims.</i></p> <p><b>Date of publication of the amended claims:</b> 20 November 1997 (20.11.97)</p>	

(54) Title: DROP-IN SUBSTITUTES FOR 1,1,1,2-TETRAFLUOROETHANE (R-134a) REFRIGERANT

**(57) Abstract**

A group of refrigerant fluids that may be combined in novel ways to produce several excellent "drop-in" substitutes for R-134a refrigerant. Performance is increased by constructing a zeotropic mixture of refrigerants, such that a single boiling point (of R-134a) is replaced by a "temperature glide" between the mixture's "bubble point" and "dew point". The temperature glide causes the phase change area in the condenser to be larger than with a single component refrigerant such as R-134a, thereby increasing heat rejection of the condenser, which lowers head pressures, and increases capacities and efficiencies compared to R-134a. Components are also selected to attempt to reduce the overall critical temperature of the mixture of refrigerants, also increasing performance and lowering head pressures under hot conditions with undersized condensers. Finally, a small amount of a mineral oil miscibility improver may be added, not to return mineral oil from the evaporator as in R-12 systems, but to keep waxes, tars, and other contaminants in the system that may have arisen from the manufacturing process (such as wax coatings on the motor windings in a hermetic compressor, or "tar" from valve packing) soluble.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**AMENDED CLAIMS**

[received by the International Bureau on 30 September 1997 (30.09.97);  
original claims 10-12 amended; remaining claims unchanged (2 pages)]

6. The mixture of refrigerants of claim 1 in which heptafluoropropane is present in about 45 weight percent, 1,1-difluoroethane is present in about 15 weight percent, and pentafluoroethane is present in about 40 weight percent.

5 7. The mixture of refrigerants of claim 1 in which heptafluoropropane is present in about 45 weight percent, 1,1-difluoroethane is present in about 20 weight percent, and pentafluoroethane is present in about 35 weight percent.

8. A mixture of refrigerants that is a drop-in substitute for  
10 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 75 weight percent heptafluoropropane, and about 25 weight percent pentafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

15 9. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 1 weight percent isobutane, about 75 weight percent heptafluoropropane, and about 24 weight percent pentafluoroethane, with the weight percentages of said components being  
20 weight percentages of the overall mixture.

10. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 1 weight percent isobutane, about 22 - 57 weight percent heptafluoropropane, about 22 - 32 weight percent

pentafluoroethane, and about 10 weight percent 1,1,1,2-tetrafluoroethane, with the weight percentages of said components being weight percentages of the overall mixture.

11. The mixture of refrigerants of claim 10 in which isobutane is present in about 1 weight percent, heptafluoropropane is present in about 67 weight percent, pentafluoroethane is present in about 22 weight percent, and 1,1,1,2-tetrafluoroethane is present in about 10 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

12. The mixture of refrigerants of claim 10 in which isobutane is present in about 1 weight percent, heptafluoropropane is present in about 57 weight percent, pentafluoroethane is present in about 32 weight percent, and 1,1,1,2-tetrafluoroethane is present in about 10 weight percent, with the weight percentages of said components being weight percentages of the overall mixture.

13. A mixture of refrigerants that is a drop-in substitute for 1,1,1,2-tetrafluoroethane refrigerant in 1,1,1,2-tetrafluoroethane refrigeration systems, comprising about 48 - 58 weight percent 1,1,1,2,2-pentafluoropropane, about 41 - 51 weight percent pentafluoroethane, and about 1 weight percent propane, with the weight percentages of said components being weight percentages of the overall mixture.

14. The mixture of refrigerants of claim 13 in which 1,1,1,2,2-pentafluoropropane is present in about 58 weight percent, pentafluoroethane is present in about 41 weight percent, and propane is